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负载钌、钯催化剂上乙酰丙酸及对乙酰氨基苯酚选择加氢的研究

Studies on Selective Hydrogenation of Levulinic Acid and Paracetamol over Supported Ruthenium and Palladium Catalysts

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摘　要

本论文以重要的生物质平台化合物乙酰丙酸（LA）加氢制备 γ-戊内酯（GVL）以及对乙酰氨基苯酚选择加氢制备酮为目标，针对选择性加氢的控制，系统研究了碳材料负载钌催化剂上乙酰丙酸加氢性能及硅烷化改性 SiO_2 负载钯基催化剂上对乙酰氨基苯酚的加氢性能。通过对催化剂的结构和性质进行较为系统的表征并与其催化活性进行关联，取得了以下主要结果。

论文针对 LA 选择加氢制备 GVL 的研究，比较了不同载体，包括不同碳材料及无机氧化物负载钌催化剂的反应性能。实验结果显示，反应产物 GVL 选择性均较高，达到 99 %以上，而载体对钌基催化剂的 LA 加氢活性具有显著影响。不同碳材料物化性质如比表面积、孔结构、电子性质及表面化学性质等都不同，对应催化剂的催化反应活性也不尽相同。因此，我们研究不同碳材料（石墨、氧化石墨、还原性氧化石墨烯、碳纳米管、碳纤维、活性炭）对 Ru 基催化剂 LA 加氢性能的影响。TEM、CO 化学吸附热等测试表明，当 Ru 金属颗粒尺寸为 1.2-2.9 nm 之间时，乙酰丙酸加氢反应是结构敏感反应，Ru 粒子尺寸越小，LA 加氢的 TOF 越高，且表面低配位的 Ru 有利于加氢反应的进行。氮气吸脱附实验及热重结果表明，载体的表面含氧官能团数量不同时，由于官能团与前驱盐之间的相互作用不同，影响金属颗粒大小，从而改变了 LA 加氢转化频率（TOF）。

另一方面，考虑到 La 在加氢反应中起到促进作用，而对 La 参与反应的机理研究仍然较少，我们将催化剂的 Ru 金属负载量降低为 1 %，提高 LA/Ru 底物比，在 100 °C、5 MPa 氢压反应条件下，考查了不同 La 助剂添加量对碳纤维负载 Ru 的 LA 加氢性能的影响。结果表明，La 含量为 0.5 %的 Ru0.5La/CF 催化剂表现出最高的 GVL 收率，是未添加 La 助剂的 Ru/CF 催化剂的 2.6 倍。当 La 的添加过量时，LA 加氢活性有所下降。利用 CO 化学吸附、CO_2-TPD、H_2-TPR、XPS、TEM 等手段研究催化剂的结构和性质，表征结果显示，在 Ru 粒径大小基本一致（2 nm 左右）的情况下，La 物种负载在 Ru/C 表面后，降低了 Ru 金属的 CO 化学吸附量。La 物种与 Ru 纳米粒子之间的相互作用促使金属 Ru 电子富集，从而有利于电子反馈到 LA 的羰基轨道上，进而促进其加氢反应的进行。同时，富集在金属 Ru 周围的碱性 La 物种易吸附反应物乙酰丙酸，从而提升 Ru 活性位

对羰基的亲核进攻能力。催化剂表观加氢活性取决于Ru活性位点数目及由Ru-La界面相互作用等因素决定的TOF值。

由于在香料、医药等领域的重要应用，苯酚类化合物选择性加氢制备相应的酮、醇化合物一直以来都受到广泛关注。对乙酰氨基环己酮是合成麻醉药吗啡及噻唑类化合物，如治疗帕金森氏病的药物普拉克索等药物的重要中间体。论文针对乙酰氨基苯酚选择性加氢制备对乙酰氨基环己酮的反应，通过调变 Pd/SiO_2 催化剂表面化学性质来改变其催化选择加氢性能。

以浸渍氨丙基三乙氧基硅烷（APTES）的方法来调变载体 SiO_2 的表面结构，通过调控催化剂焙烧温度改变催化剂上硅烷化官能团的含量。TEM 结果表明，在 Pd 金属粒子大小为 4-7 nm 范围内，催化剂加氢活性与金属颗粒大小相关性低。硅烷化试剂 APTES 使载体表面存在一定量的官能团，而硅烷化官能团的含量影响对乙酰氨基苯酚加氢反应活性及酮的选择性。从 H_2-TPR 结果可知，由于催化剂焙烧温度不同，催化剂还原能力及 Pd-H 物种稳定性均有所不同。对于 500 ^oC 焙烧后的 Pd/Sily-500 催化剂，Pd-H 物种分解温度较低，H_2 与 Pd 之间吸附较弱，易脱附的氢更有利于加氢反应的进行。当 H 原子在 Pd 表面难脱附时，不易参与加氢反应，导致催化活性较低。官能团的存在改变了 Pd 物种在载体表面的存在状态，硅烷化处理后 Pd 催化剂表面更易形成 PdH 物种，因此提高了 Pd/SiO_2 催化剂的加氢活性。另一方面，对乙酰氨基苯酚通过苯环 π 电子结构吸附在催化剂 Pd 金属上进行反应，反应底物平面及非平面两种吸附方式影响了反应选择性的大小。硅烷化试剂的存在增强了反应的空间位阻效应，即表面官能团的存在阻碍了对乙酰氨基苯酚与催化剂之间通过 Pd-O 键的平面吸附，进而阻止了其进一步加氢反应，从而显著提高酮的选择性。对于未进行硅烷化处理的 Pd/SiO_2 催化剂，反应物更倾向于以共平面吸附方式存在于催化剂表面，随后进行深度加氢生成对乙酰氨基环己醇。

关键词： 乙酰丙酸；戊内酯；对乙酰氨基酚；对乙酰氨基环己酮；选择加氢

Abstract

This dissertation focused on the studies of the hydrogenation of levulinic acid (LA), a key platform compound from cellulose, into γ-valerolactone (GVL) and the selective hydrogenation of paracetamol into 4-acetamidocyclohexanone.

For the hydrogenation of LA, the catalytic performances of Ru nanoparticles loaded on the various supports were investigated in aqueous solutions, including the different oxide supports and carbon supports. It was found that the selectivity of GVL over Ru catalysts could reach 99 %, and the activity of the catalysts was affected significantly by their supports. Physicochemical properties of carbon materials, such as electrical conductivity, surface area and porosity, and chemical properties could be tuned for specific applications. Few reports deal with the influence of carbon characteristics such as nanostructure and surface chemical properties on the performance of the carbon supported Ru catalysts for the synthesis of γ-valerolactone from levulinic acid. Herein, the present work focuses on the Ru supported on very different carbon materials and their influences on the LA hydrogenation reaction. Ru-catalyzed hydrogenation of LA was a structure-sensitive reaction when the Ru particle size changed within 1.2-2.9 nm, small Ru nanoparticles favor the transformation of LA and the turnover frequency increased with decreasing the mean size of Ru nanoparticles. The test results of intrinsic activity and TOF in the LA hydrogenation reaction suggests that the low-coordination unsaturated Ru sites at the small metal nanoparticles are responsible for the improvement of catalytic activity. The characterizations by means of BET, TG were conducted and the results indicated that the amount of oxygen groups varied with support kinds, leading to a different Ru particle size. The differential heats of CO adsorption do not depend on the oxygen-contained groups, which were relevant to the particle sizes and electron density of ruthenium.

On the other hand, the incorporation of lanthanum on carbon nanofiber supported

Ru catalyst (a lower Ru loading) and its influence on the catalytic activity for the hydrogenation of LA to GVL was also studied in this work according the few study on the mechanism of the influence of La addition. Concerning the catalytic activity, at a temperature of 100 ^{o}C, hydrogen pressure of 5 MPa, the optimized Ru0.5La/CF catalyst afforded 2.6 times GVL yield than the monometallic Ru catalyst. A maximum in the reaction rate (53.8 μmol·gRu^{-1}·min^{-1}) is noted upon increasing La content (Ru0.5La/CF), followed by a decline in catalytic activity at the lanthanum level in excess of the maximum. The satellite/main peak intensity ratio (I_{sat}/I_{mp}) from La $3d_{5/2}$ XPS spectra and TPR results indicated the presence of Ru interacting with La and the lanthanum was present in a different chemical environment. The shift of metallic Ru 3d peak positions to lower binding energy indicated the enhancement of electron density of Ru species by La addition to Ru/CF. Turnover frequencies for LA hydrogenation on RuLa/CF catalysts were found to increase with the addition of La mole fraction, suggesting the improvement of the surface Ru-La interfaces in the reactivity. Therefore, the catalytic performance was a consequence of both Ru metal which might be blocked by the dopant La and the Ru-La interfacial sites.

The hydrogenation of substituted phenols to the corresponding alkyl-substituted cyclohexanones and cyclohexanols has generated great interest in the industry and researchers, due to their application in the subsequent manufacture of fine chemicals for the fragrance and detergent industries. The 4-acetamidocyclohexanone was prepared as an intermediate in the synthesis of morphine skeleton. Nevertheless, reports on the produce of 4-acetamidocyclohexanone are still limited. Herein, in the present work, we attempt to tune the surface chemical composition of heterogeneous metal catalysts to optimize their hydrogenation performances.

For this, the silylated SiO_2 was prepared by impregnation of silica gel with the (3-aminopropyl) triethoxysilane (APTES) solution in toluene. The amount of sily groups on the SiO_2 support was tuned via the temperature of calcinations. TEM characterization indicated that the specific activity of catalyst did not seem to be greatly affected by the particle size considering the narrow size range of Pd particles (4-7 nm). From TPR results, the reducing ability of the catalysts and the stability of

the hydride phase could be tuned by the various calcination temperatures. The silylation process favors the formation of hydride phase on the Pd catalyst. Moreover, the palladium hydride species decompose at a lower temperature on the Pd/Sily-500, indicating a weaker absorption of H_2 on a Pd, which can facilitate the hydrogenation activity. Meanwhile, the APTES anchored on the support impedes the planar adsorption of paracetamol via O-Pd bonding on the catalyst surface due to steric hindrance, thus preventing them from further hydrogenation. The non-silylated SiO_2 supported Pd catalyst favors the co-planar absorption of paracetamol, obtaining the deeply hydrogenated product of 4-acetamidocyclohexanol.

Keywords: levulinic acid; γ-valerolactone; paracetamol; 4-acetamidocyclohexanone; selective hydrogenation